Filling control of the pyrochlore oxide $Y_2Ir_2O_7$

Hideto FUKAZAWA[1,*] and Yoshiteru MAENO[1,2]

[1] *Department of Physics, Kyoto University, Kyoto 606-8502*
[2] *International Innovation Center, Kyoto University, Kyoto 606-8501*

(Received February 1, 2008)

KEYWORDS: $Y_2Ir_2O_7$, pyrochlore, Mott insulator, metal-insulator transition, iridate, filling control

Recently pyrochlore iridates, $R_2Ir_2O_7$ (R = Y and lanthanides), have provided additional research interests in geometrically frustrated magnetic systems.[1,2,3] These materials were reported as early as about 30 years ago but were little studied.[4] Kennedy *et al.*[5] studied the crystal structure of the materials, but they have not reported the low-temperature properties, which are essential for the characterization of the frustrated magnetic systems.

The magnetic frustration arises because of the pyrochlore structure in which R and Ir sub-lattices form individual networks of linked tetrahedra. Systematic variations of the physical properties have been investigated by changing the elements of the R site.[1] Furthermore, one may expect that each Ir ion has a quantum spin $S = 1/2$ if the 5 $5d$ electrons in the t_{2g} orbitals are localized in the presence of strong electronic correlation. Although a quantum spin liquid state is theoretically expected for antiferromagnetic Heisenberg pyrochlore magnet,[6] there have been few candidates of the actual materials studied up to now. Besides, Fujimoto[7] theoretically showed for a hole-doped pyrochlore Mott-insulator based on an s-electron system that the electronic specific-heat coefficient γ exhibits a divergent behavior near the boundary of metal-insulator transition. These urge us to study the $S = 1/2$ pyrochlore system, pyrochlore iridates.

Of the pyrochlore iridates, $Y_2Ir_2O_7$ serves as a reference material, since it does not possess a magnetic rare-earth element on the R site and its physical properties are comparable with those of its isomorphs $Y_2Mo_2O_7$[8] and $Y_2Ru_2O_7$,[9] based on $S = 1$.

$Y_2Ir_2O_7$ exhibits non-metallic behavior down to 4.2 K and exhibits quite a small ferromagnetic (FM) component below T_m = 170 K, though it has not been well understood whether such FM component is intrinsic or not.[1,2] In spite of the non-metallic behavior, it has been reported by Taira *et al.*[2] that the γ is finite, 4.1(3) mJ/K^{2}mol-Ir, suggesting the existence of the Fermi surface. We will discuss the origins of the finite γ and the FM component of $Y_2Ir_2O_7$. It is vital to investigate the filling control of $Y_2Ir_2O_7$ in order to search for the metallic phase adjacent to the strongly correlated nonmetallic phase. We succeeded in synthesizing hole-doped material, namely $Y_{2-x}Ca_xIr_2O_7$ (x = 0.2, 0.3, 0.4 and 0.6). As the main purpose of this note, we will show the metal/non-metal (M/NM) crossover and the enhancement of the γ in $Y_{2-x}Ca_xIr_2O_7$.

We used polycrystals synthesized by the conventional solid-state-reaction method.[1] We measured the resistivity by a standard four-probe method below 300 K and the specific heat by a relaxation method between 1.8 and 300 K (Quantum Design, PPMS). We investigated the dc magnetization with a SQUID magnetometer (Quantum Design, MPMS$_{5S}$) between 1.8 and 350 K.

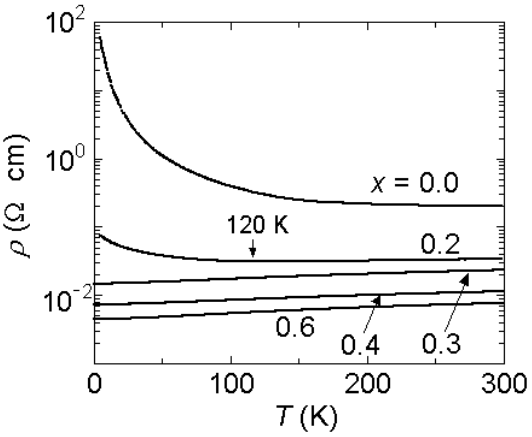

Fig. 1. Resistivity of $Y_{2-x}Ca_xIr_2O_7$.

The lattice parameters at room temperature depend little on x (a = 10.184(2)Å, cubic) except for x = 0.0 (a = 10.176(1)Å, cubic). We note that transport properties at room temperature also change from non-metallic to metallic between x = 0.0 and 0.2.

In Fig. 1, we plot the resistivities of $Y_{2-x}Ca_xIr_2O_7$. $Y_2Ir_2O_7$ exhibits non-metallic behavior, as we previously reported.[1] For x = 0.2, it exhibits metallic behavior down to about 120 K, and non-metallic behavior at lower temperature. For x = 0.3, 0.4 and 0.6, it exhibits metallic behavior at least down to 0.3 K; however, no sign of superconductivity has been observed.

In Fig. 2, we plot the dc magnetic susceptibilities $M(T)/H \equiv \chi(T)$ ($\mu_0 H$ = 1 T). Very small FM component, amounting to 4×10^{-3} of the saturated moment of $S = 1/2$ spins, is observed for x = 0.0 (T_m = 170 K) and 0.2 (T_m = 100 K). The T_m of $Y_2Ir_2O_7$ is consistent with the value previously reported by us[1] and by Taira *et al.*[2] The FM component was not observed above x = 0.3. Thus, the magnetic ground state appears to be correlated with non-metallic ground state. We obtained the effective spin $S_{eff} = 0.07(1)$ from the Curie-Weiss fitting ($\chi(T) = \chi_0 + \frac{4\mu_B^2 S_{eff}(S_{eff}+1)}{3k_B(T-\theta_{CW})}$) for $Y_2Ir_2O_7$ above T_m. It corresponds to only 14(2)% of the expected spin $S = 1/2$.

Small magnetic moment of $Y_2Ir_2O_7$ below T_m may be due to either spin-glass ordering or canted antiferromagnetic ordering. Since no anomaly was observed at around T_m in specific heat (data not shown), the FM component is attributable to spin-glass ordering as previously reported in other pyrochlores, such as $Y_2Mo_2O_7$[8] and

* E-mail address: hideto@scphys.kyoto-u.ac.jp

$Y_2Ru_2O_7$[9].

We should note that an additional steep increase of magnetization was observed for all the materials with decreasing temperature below about 15 K. Since no change in $\rho(T)$ was observed below this temperature, the increase is attributable to magnetic impurities or Ir spins at grain boundaries.

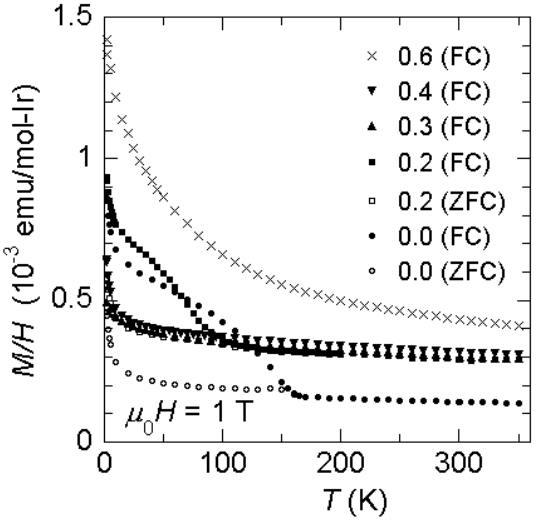

Fig. 2. Magnetic susceptibilities of $Y_{2-x}Ca_xIr_2O_7$. Solid symbols denote the data obtained after field-cooling. Open symbols denote the data obtained after zero-field-cooling.

In Fig. 3, we plot the specific heat divided by temperature, $C_P(T)/T$, against T^2. Solid line for $x = 0.0$ denotes the quadratic fitting, $C_P/T = \gamma + \beta T^2$, between 14 and 20 K. Below 14 K, it is difficult to perform a valid quadratic fitting because of additional increase of C_P/T with decreasing T.[10] This increase cannot be explained in terms of the localization effect, since in a such case C_P/T should exhibit linear behavior (the Debye T^3 term) with finite intercept γ at least up to 20 K. We speculate that the origin of the increase is attributable to a magnetic contribution, since it appears to correspond to the steep increase of $\chi(T)$ below 15 K.

Although C_P/T of $Y_2Ir_2O_7$ at 1.8 K is 5.8(2) mJ/K^{2}mol-Ir, we may consider that the γ, which is equal to 0.0(5) mJ/K^{2}mol-Ir, is the intrinsic γ. This value strongly suggests that $Y_2Ir_2O_7$ is a Mott insulator.

In the inset of Fig. 3, we show the γ against the substitution content x. The γ is obtained from the quadratic fitting between 14 and 20 K. We note that the Debye temperature is $\Theta_D = 400(10)$ K and depends little on x. Once additional holes are introduced into the half-filled t_{2g} band, the finite density of states at the Fermi level appears. The γ for $x = 0.2$ is 8.1(5) mJ/K^{2}mol-Ir much greater than the value, 1(1) mJ/K^{2}mol-Ru, for the corresponding material $Y_{1.8}Bi_{0.2}Ru_2O_7$.[9] With increasing x across the M/NM boundary, γ nearly monotonically increases without clear divergent behavior. This is in contrast with the behavior in $Y_{2-x}Bi_xRu_2O_7$, for which γ takes a sharp maximum at the metal-insulator boundary.[9] In order to explain the apparent discrepancy between our results and the theory based on an s-electron,[7] we should take into account of the role of $5d$ electrons, which give rise to more complicated band structure compared with that of s electrons.

In summary, we have revealed that $Y_2Ir_2O_7$ is a Mott insulator. We have also shown that the density of states at the Fermi level rapidly changes with x by the filling control of $Y_2Ir_2O_7$. The magnetic ground state appears to occur concomitantly with non-metallic state.

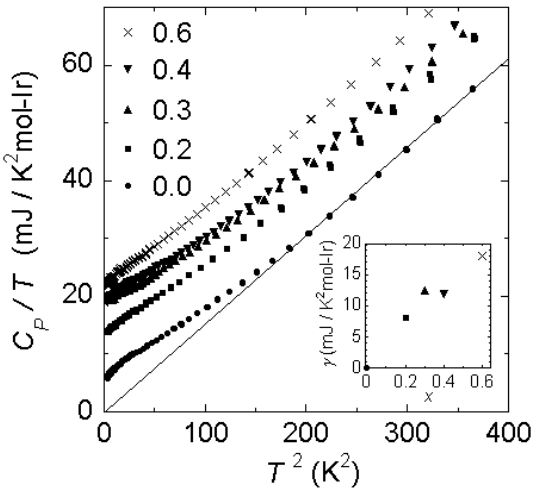

Fig. 3. Specific heat divided by temperature against squared temperature below 20 K. Solid line denotes the quadratic fitting between 14 and 20 K. Electronic specific-heat coefficient against the substitution content (inset).

The authors acknowledge D. Yanagishima for his contributions. They would like to thank T. Ishiguro for his support. They appreciate stimulating discussion with R. Higashinaka, M. Sato, S. Fujimoto and H. Tsunetsugu. H. F. acknowledges financial support from JSPS Research Fellowships for Young Scientists. This work has been supported by the Grant-in-Aid for Scientific Research(S) from the Japan Society for Promotion of Science, by the Grant-in-Aid for Scientific Research on Priority Area "Novel Quantum Phenomena in Transition Metal Oxides" from the Ministry of Education, Culture, Sports, Science and Technology, and by a Grant from CREST, Japan Science and Technology Corporation.

[1] D. Yanagishima and Y. Maeno: J. Phys. Soc. Jpn. **70** (2001) 2880.
[2] N. Taira, M. Wakeshima and Y. Hinatsu: J. Phys.: Condens. Matter **13** (2001) 5527.
[3] S.T. Bramwell and M.J.P. Gingras: Science **294** (2001) 1495.
[4] M.A. Subramanian, G. Aravamudan and G.V.S. Rao: Prog. Solid St. Chem. **15** (1983); and references therein.
[5] B.J. Kennedy: Physica B **241-243** (1998) 303.
[6] B. Canals and C. Lacroix: Phys. Rev. Lett. **80** (1998) 2933.
[7] S. Fujimoto: Phys. Rev. B **64** (2001) 085102.
[8] N. P. Raju, E. Gmelin and R. K. Kremer: Phys. Rev. B **46** (1992) 5405.
[9] S. Yoshii and M. Sato: J. Phys. Soc. Jpn. **68** (1999) 3034.
[10] N. Taira *et al.* (Ref. 2) indeed performed the quadratic fitting by using the data only below 6 K.